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SYNTHESIS OF NOVEL FLUORINE COMPOUNDS: NEW EXPERIMENTAL

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CHEMISTRY R J LAGOW 31 MAY 82 AFOSR-TR-82-1037

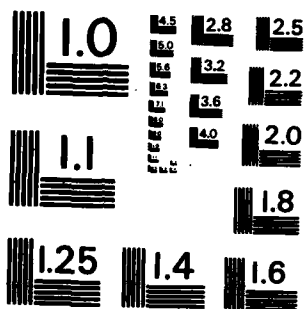
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COMPLETED PROJECT SUMMARY

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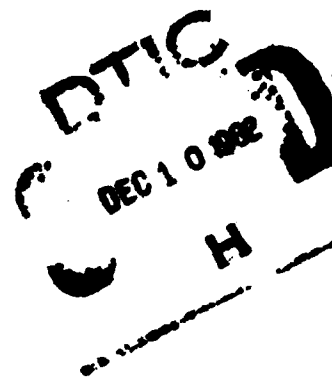
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8. PUBLICATIONS:

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The direct fluorination techniques which we have developed in our laboratory at M.I.T. and at the University of Texas over the past several years have developed into a mature and useful synthetic technique. We believe that the synthetic work accomplished recently in our laboratory and in other laboratories in the United States, Europe and Japan has established that direct fluorination is the most generally applicable technique for the synthesis of novel fluorine compounds. That is to say, in cases where there is not an established industrial process for preparation of the new fluorine containing species, direct fluorination has the highest probability of synthetic success. Presently, the major exception is for partially fluorinated organofluorine compounds. It has also been clearly established that there are large numbers of classes of compounds for which direct fluorination is presently the only satisfactory synthetic approach. Industry is now beginning to recognize these advantages inspite of the formidable technological changes which will be required to utilize direct fluorination on an extremely large scale.

The importance of direct fluorination is further enhanced by the simple fact that it has been demonstrated over the years that fluorine compounds are among the most useful classes of synthetic materials known. Academically, in the pursuit of strange phenomena, fluorine compounds also have a strong track record, exhibiting many extreme properties including stability in some cases and extreme reactivity in others. It would, therefore, follow that direct fluorination should be fully developed and exploited. Industrial interest in direct fluorination in Japan could be described, at present, as intense with substantial amounts of money going into research. University and academic interest is also developing. In the United States, Air Products has new commercial ventures involving direct fluorination technology and Allied Chemical has indicated that it is establishing such commercial facilities for the synthesis of hexafluoroacetone.

We are in the midst of preparing a series of highly branched ethers and feel that the significance of this series of compounds in terms of new materials applications warrants a very intensive investigation of their synthesis and properties. The highly branched ethers are thermally stable even beyond the more linear perfluoro polypropylene oxide and polyethylene oxide structures which are now marketed by DuPont and Montedison. Thermal analysis shows that some of the branched polyethers are stable to about 420°C which is considerably more than the 360°-380°C which is standard for polytetrafluoroethylene. Further, when these highly branched

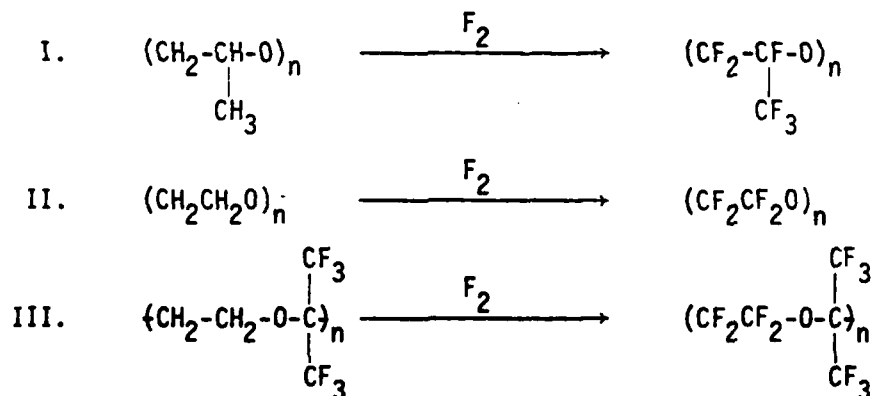
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MATTHEW J. KERPER
Chief, Technical Information Division

perfluoropolyethers decompose, they do not carbonize as does polytetrafluoroethylene but rather, depolymerize into shorter chain perfluoropolyether segments. Their specific decomposition products are the subject of current investigation in our laboratory.

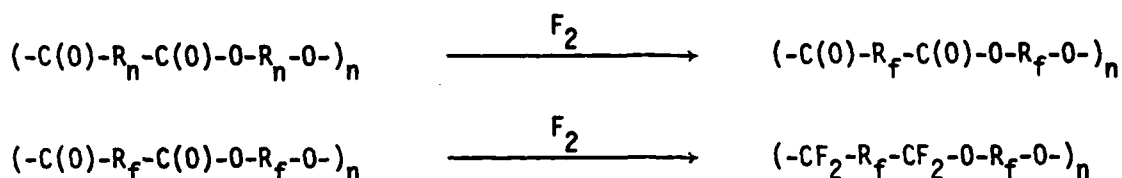
Our tentative explanation for the increased thermal stability is the fact that such highly branched structures make poor thermal contact with a heated surface. The vibrational excitation the oligomer or polymer received from contact with heated surfaces must be transferred successively through (perhaps four sigma bonds) bonds in order to vibrationally excite the backbone fluorocarbon chain. Thus, the fluorocarbon chain does not make direct contact with a thermal environment. The polymeric materials appear to survive without visible decomposition even beyond the limit of their thermal temperature stability. We are also interested in their novel shape and its effect on lubrication properties. Fluorocarbon polymers, in general, have a low coefficient of friction, but highly branched fluorocarbons will make even less contact with surfaces and that contact is made as in the case of other fluorocarbons with the sheet of non-bonding electrons characteristic of protruding fluorine atoms. As we mentioned before, perfluoropropylene oxides and ethylene oxides are now commercial products. They are sold for approximately \$100 to \$300 per pound. We have previously studied the fluorination of the hydrocarbons polyethylene oxide and propylene oxide.¹⁻⁴ Lower molecular weight perfluorocarbon polyethers are prepared from the high polymer systems by high temperature fragmentation in elemental fluorine.¹⁻⁴



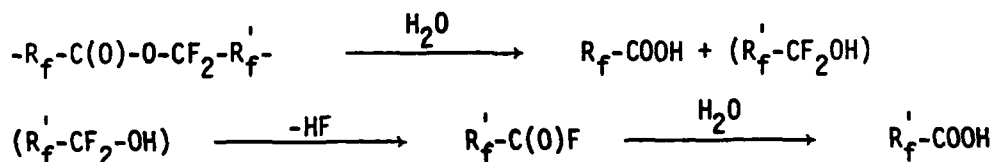
We have succeeded in making oils, greases, waxes and species of almost any molecular weight desired, including high polymers, from such direct fluorination reactions. We now think that this is a less expensive method for making perfluoropolyether oils and greases and we may have convinced a Japanese chemical company recently to go into production of polyethers using this technology. We think the prospects for Air Products Corporation marketing the materials is also good. Fluorine costs only \$6.00 a pound and the hydrocarbon precursor polymer costs on the order of 30¢ a pound. Beating a \$100 per pound price proposes no great difficulty.

It is, however, synthesis of other structures such as highly branched perfluoropolyethers, unsymmetrical perfluoropolyethers, and longer carbon chain perfluoropolyethers where direct fluorination provides a unique synthetic approach. For example, the polymerization of epoxides produces only a repeating chain polyethers and if one wants an AB or an ABC polyether structure, the use of a polyester as a starting material is quite an advantage. In fact, there are only about fourteen commercially produced hydrocarbon polyether starting materials. With a new technique to be discussed in the next section, the number of new materials it is possible to produce in the perfluoropolyether area is almost unlimited.

The synthetic scheme which is being used to explore the perfluoropolyethers from hydrocarbon polyesters is:



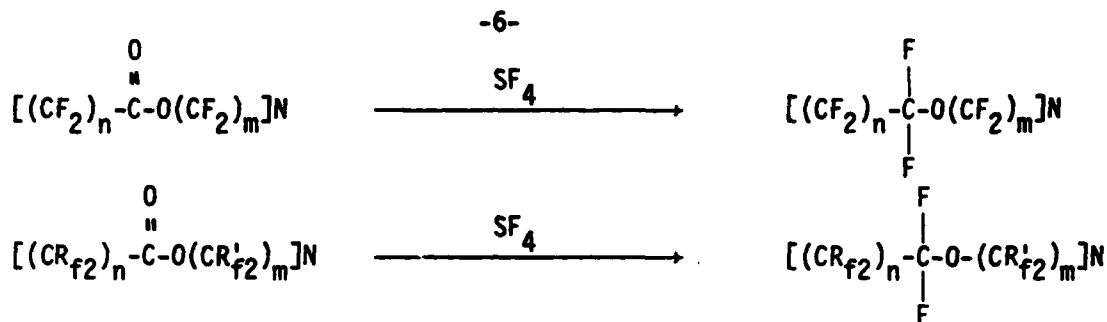
Perfluoroesters are interesting compounds in their own right, and production by direct fluorination, isolation and characterization of such compounds would be a significant achievement for the technique and the experimentalist. The significance of this work is seen clearly in view of the current absence of any general method for producing perfluoroethers. Perfluoroesters, however, are not of great interest for practical applications; the electron withdrawing perfluoro substituents cause the ester linkage to be extremely susceptible to hydrolysis, even by atmospheric moisture. Each perfluoroester linkage would be hydrolyzed by two molecules of water to two carboxylic acid end-groups as follows:



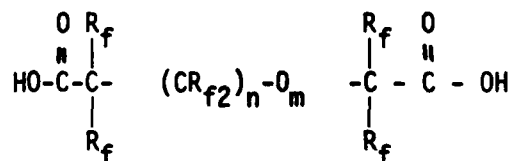
The resulting perfluoropolyesters oligomers have been treated with sulfur tetrachloride to convert the carboxylic acid groups to CF_2 groups thus rendering a perfluoropolyether. We have done this with nonstoichiometric amounts of SF_4 such that there will be left in the structure a number of unreacted ester linkages. The system is then hydrolyzed (perfluoroesters hydrolyze spontaneously) to produce difunctional perfluoro polyesters with the following structures:



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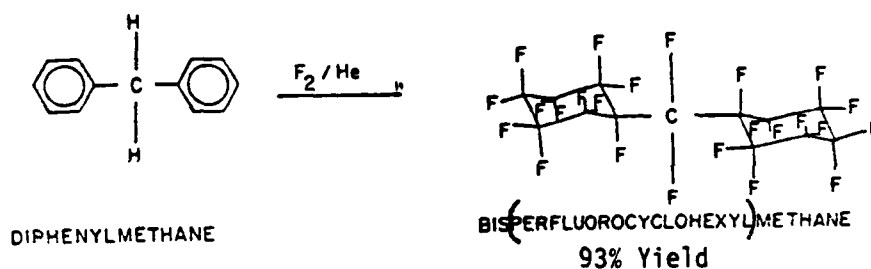
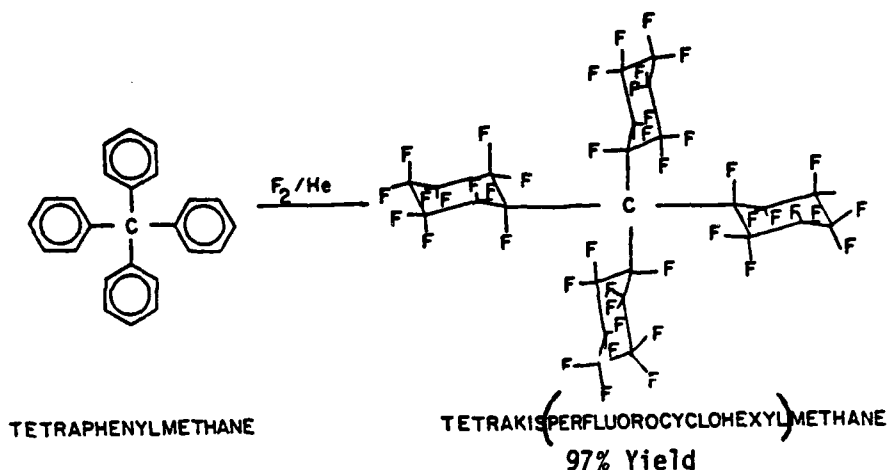
Thus hydrolysis of the remaining ester groups will lead to the isolation of perfluorocarbon ether diacids:



It is clear from the work underway that with an excess of sulfur tetrafluoride, very high molecular weight polymers are obtained. With a lesser amount of SF_4 one can vary the average chain length of difunctional branched polyethers almost at will. Applications of such difunctional perfluoropolyethers are treated in a subsequent section in a discussion of prospects of co-polymer chemistry.

It is also possible to prepare oils, greases, and waxes with appropriate chain lengths by either high temperature fragmentation in fluorine of the high molecular weight polymer systems or by direct fluorination and removal of the end group from the shorter chain difunctional oligomers. A number of such lower molecular weight difunctional oligomers are now being characterized. It should not go unnoticed that the highly branched nature of these polymers destroys crystallinity and makes them excellent pure fluorocarbon elastomers.

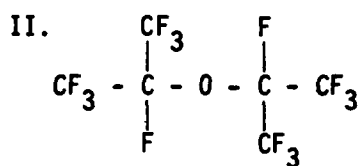
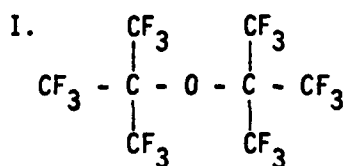
Recently in our laboratory, we have prepared two very interesting carbon-substituted methanes, tetrakis(perfluorocyclohexyl)methane and bis(perfluorocyclohexyl)methane:



These compounds were prepared because they are thought to have very advantageous steric properties for use as fluorocarbon oxygen carriers, as blood substitutes, and for other applications. The tetrakis compound is a very stable glass-like material and its appearance and stereochemistry make it interesting structurally. A single crystal X-ray study is underway.

It has occurred to us that this same general procedure should be useful for synthesis of perfluorocyclohexyl organometallic compounds most of which are not known. We have preliminary results on the reaction of fluorine with tetraphenylgermane, tetraphenylsilane, tetraphenyltin and tetraphenyllead. We are also interested in the study of perfluorocyclohexyl group III and group V elements.

We have prepared recently, by direct fluorination, and currently have under study, the perfluorocarbon polyethers:



These materials were previously unknown. Because they have steric bulk, they are thought to be of interest as oxygen carriers in the artificial blood substitute area. We have recently added five new graduate students who have indicated an interest in direct fluorination studies. With this large group of people to train, we have undertaken the synthesis of a series of about 20 structurally unusual fluorocarbon molecules that were selected primarily for their desirability as fluorocarbon blood substitutes. It is our theory that bulky substituents which create packing holes in the liquid phase are the most promising fluorocarbon blood substitutes. Therefore, the synthesis of such molecules provides training for students on relatively easy projects, not characteristic of the type of reactions we normally pursue in our research programs. These materials will be screened by Dr. Leland Clark of Cincinnati Children's Research Foundation.

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